Measurements of Condensed-Phase NOy from the WB-57F in CRYSTAL-FACE

AJ Weinheimer[1], BA Ridley[1], DJ Knapp[1], DD Montzka[1], FE Grahek[1], RG Hendershot[1], DW Fahey[2], RS Gao[2], PJ Popp[2], TP Marcy[2], EM Weinstock[3], JB Smith[3], DS Sayres[3], J Vellovic[3], JG Anderson[3], D Baumgardner[4], BE Anderson[5], TP Bui[6], SW Bowen[6], L Pfister[6], J Dean-Day[6], C Chang[6]
[1]NCAR, Boulder, CO; [2]NOAA, Boulder, CO; [3]Harvard U., Cambridge, MA; [4]UNAM, Mexico City; [5]NASA-LaRC, Hampton, VA; [6]NASA-Ames, Moffett Field, CA

NCAR

Introduction: Reactive nitrogen species (NO_y) are central to the chemistry of ozone in the atmosphere. Their interconversions, their removal from the gas phase to particles, and their return to the gas phase from particles are important aspects of their cycling in the atmosphere. HNO_3 is known to be taken up by ice particle and ternary solution aerosols, and other NO_y species may also be taken up, so a goal of CRYSTAL-FACE was to measure the condensed-phase amounts of HNO_3 and NO_y on ice and other particles. On the WB-57, the NO_y and HNO_3 instruments were both equipped with similar pairs of inlets so that each would have a forward-facing inlet to collect particles in an enhanced manner (enhancing the particle signal relative to that from the gas phase), plus a second inlet to collect primarily gas-phase only. For HNO_3 this second inlet was downward-facing, for NO_y it was in fact forward-facing, but shielded from particles larger than ~4 μm in diameter by its placement on the aft of an airfoil. Thus the difference signal ("fore" minus "aft") for NO_y is sensitive to particles larger than ~4 μm, while for HNO_3, the sensitivity of the difference signal extends to smaller sizes, although the enhancement factor is decreased from its high-mass limit at smaller sizes (<10 μm). For this poster, the calculations of the condensed-phase amounts, expressed as the gas phase equivalents NO_y-coPh and HNO_3-coPH, were accomplished by assuming the high-mass limit enhancement factor. To calculate the particulate surface density of NO_y or HNO_3 (molecules per unit surface of particle area), the CAPS instrument was used (CIP for particle diameters larger than 50 μm, CAS for smaller). This calculation is appropriate if the NO_y or HNO_3 is distributed over the surface of the particles. To calculate the condensed-phase mixing ratio (NO_y/H_2O) for ice particles, as if the NO_y were distributed throughout the volume of the particles, Harvard ice water content was used (it is also used to correct the sensitivity of the NO_y-fore channel for its H_2O-dependence).

2002 0721: As the WB57 circled (Fig. 1a, 21:53-21:59), it made two passes into a cloud at 12.6 km and **T = 213 K**. The satellite photo shows that these samples were at the edge of, or even outside of, the visible anvil, but the elevated levels of NO (Fig. 1b) indicate that this was likely air in which the ice particles had evaporated for the most part. Both the NO_y and HNO_3 instruments saw condensed-phase species in these passes (Fig. 1c) with the condensed-phase HNO_3 being about twice the condensed-phase NO_y (worse agreement than usual). Using the CAPS surface area (Fig. 1b), the NO_y-coPh per unit surface area may be compared with that predicted by the Frenkel-Halsey-Hill (FHH) model of Hudson et al. [2002] (Fig. 1c,d). In this case the FHH model gives values quite close to those measured (better agreement than most cases; see later). The surface density had maximum values of 0.2-0.5 x 10^{14} molecules of NO_y cm^{-2}, or 4-10% of a monolayer. The surface density also exhibits a variation with HNO_3 partial pressure as predicted by the FHH model; HNO_3(g) and surface density are at their minima at the centers of these passes. When expressed as if the NO_y were distributed throughout the volume of the ice, condensed-phase mixing ratios (NO_y /H_2O) of 2-10 ppmv are found, and these are greatly in excess of those predicted from the solubility of HNO_3 in ice (Fig. 1d) [Thibert and Domine, 1998]. Moreover the sensitivity of the dissolved species to gas-phase HNO_3 is much less than that observed (Fig. 1d). Using the uptake efficiencies of Hudson et al. [2002], the gas-phase lifetime of HNO_3 may be evaluated in the kinetic limit. These efficiencies are small (3-7 x 10^{-3} for 209-220 K) and can limit the uptake if surface areas are small. Values of 8-20 min are calculated for the bulk of the cloud, and these are fast enough that equilibrium is likely to be attained. Another notable feature of these passes is that the decrease in gas-phase nitric acid (~1000 pptv) exceeds the condensed-phase HNO_3 by about a factor of 2 (and the condensed-phase NO_y by even more). Assuming that the air inside the clouds is otherwise similar to that outside, as the elevated NO suggests it is all ex-anvil air, this implies a loss of HNO_3.

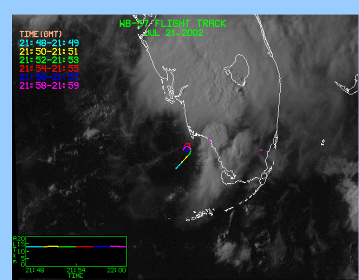

Fig. 1a

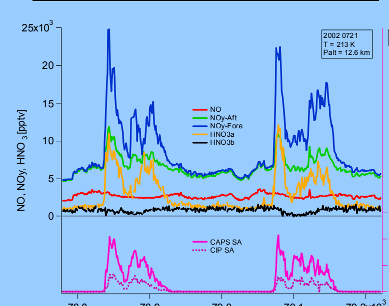

Fig. 1b

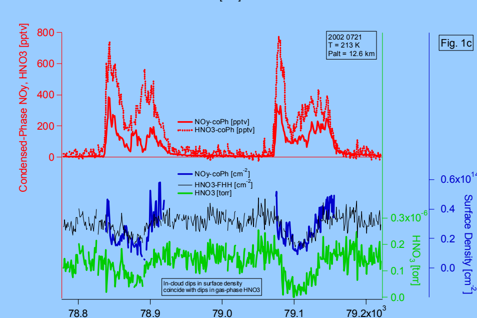

Fig. 1c

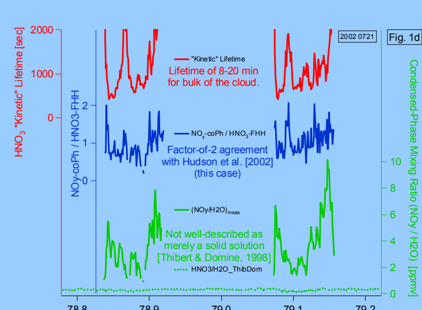

Fig. 1d

20020711: For this cloud pass at 13.1 km and **T = 208 K** (Fig. 2a, 20:07-20:10), similar amounts of NO_y-coPh and HNO_3-coPh were observed, with peak values up to ~100 pptv (Fig. 2c). The surface densities on the CAPS surface area go up to ~0.2 x 10^{14} cm^{-2}, or about 4% of a monolayer, and this is about 50% of that predicted by the FHH model (Fig. 2d). An earlier pass at 71.3 ks, 13.8 km, **T = 204 K**, (not shown) shows very similar behavior. The NO_y and HNO_3 condensed-phase amounts are in agreement with each other and the coverage is about 50% of that predicted by the FHH model, although this temperature is slightly below the range of temperatures for which the laboratory observations were made.

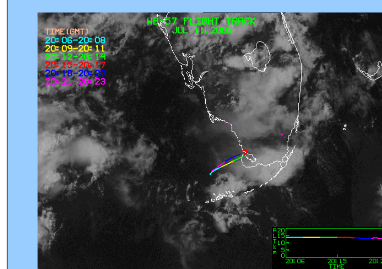

Fig. 2a

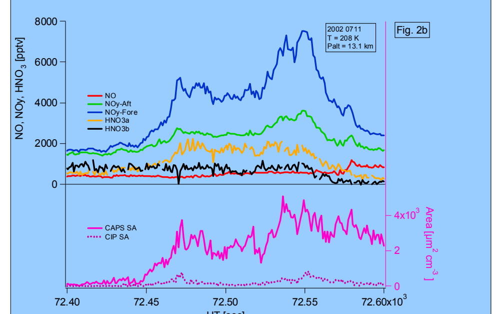

Fig. 2b

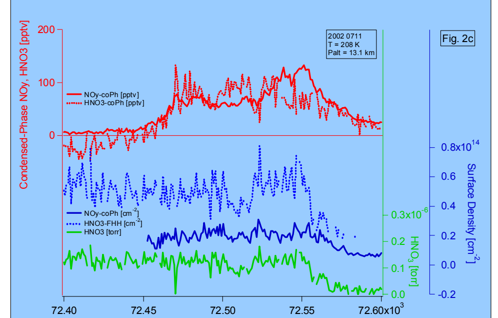

Fig. 2c

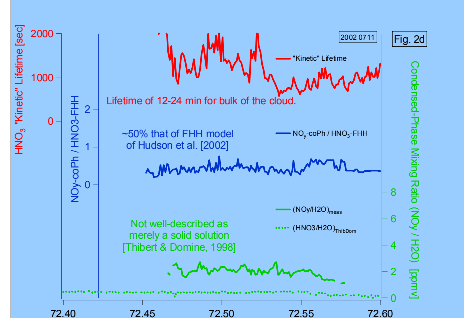

Fig. 2d

2002 0709: For this cloud pass (Fig. 3a, 18:43-18:53) during a gentle ascent from 14.4 to 14.8 km, T = 196-201 K, temperatures are cold enough to enable significant condensation of HNO_3. However, the gas-phase measurements show virtually zero HNO_3 (except around the data gap near 67.5 ks), and this is consistent with the virtually zero condensed-phase NO_y observed on ice particles in CAPS surface areas up to 10 x 10^3 μm^2 cm^{-3} around 67.8 ks (Fig. 3b). It is very striking that for both of the condensed-phase measurements, the usual correlation with the presence of ice is absent; it is also notable that most of the surface area is on particles larger than 50 μm (CIP). The very small, steady offset in NO_y-coPh, which is sensitive to sizes larger than about 4 μm, is not be distinguishable from zero (at this stage of analysis), and this suggests an absence of HNO_3 on larger (ice) particles. However, the condensed-phase HNO_3 appears to be significantly larger than zero (HNO_3a > HNO_3b in Fig. 3c), consistent with the presence of HNO_3 on small non-ice aerosols [Meilinger et al., 1999], both in and out of cloud, and the greater sensitivity of HNO_3-coPh to smaller particles. In these plots, the high-mass limit enhancement factor is assumed when deriving the gas-phase-equivalents plotted in Fig. 3b. If the HNO_3-containing particles are only a few μm in diameter, and smaller, a smaller enhancement factor should be used, leading to larger gas-phase-equivalent HNO_3, larger than the 20-30 pptv indicated. Also, it is notable that there is significant NO_y present during the time when NO_y-coPh is virtually zero, and since none of the NO_y is HNO_3 and less than half of it is NO_x, a significant fraction of it could be PAN, yet we see no condensed-phase NO_y on ice. This suggests that gas-phase HNO_3 may be necessary for the occurrence of significant NO_y on ice.

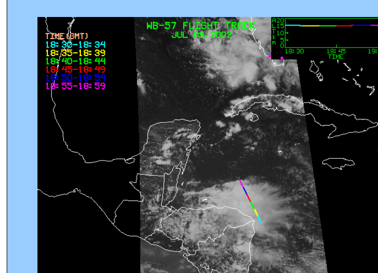

Fig. 3a

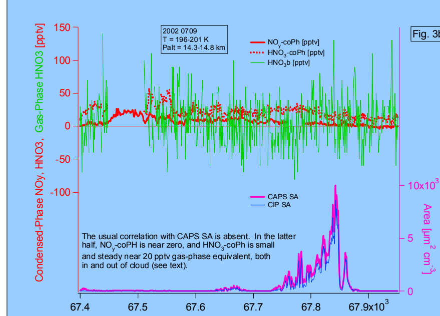

Fig. 3b

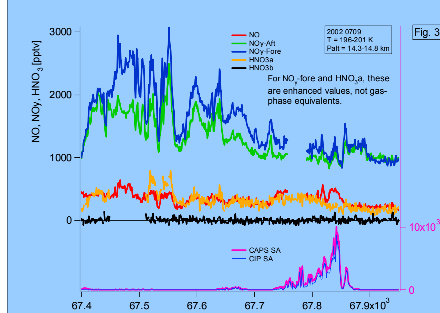

Fig. 3c

2002 0713: In subvisible cirrus at 14.4 km and **T = 198 K** (Fig. 4a, 20:56-21:10), the NO_y and HNO_3 instruments measured condensed-phase amounts of up to a little more than 100 pptv (gas-phase-equivalent), in reasonable agreement with each other. At this cold temperature, one of the largest NO_y surface densities was found among the cases studied. Values calculated for the coverage of the CAPS surface area, practically all which is on particles smaller than 50 mm (Fig. 4b, 2nd panel), are generally in the range of 1-2 x 10^{14}, or 20-40% of a monolayer. This temperature is beyond the range of the laboratory measurements on which the FHH model of Hudson et al. [2002] is based. Nonetheless, that calculation was made and the results are very noisy and not shown, but most of the values were in the range of 0.01 to 1.0 times the FHH value. A comparison is made with the solubility expression of Thibert & Domine [1998] (even though beyond its range, too), and the measured amounts greatly exceed those calculated.

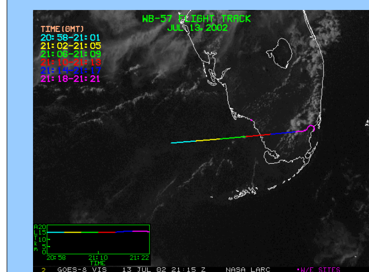

Fig. 4a

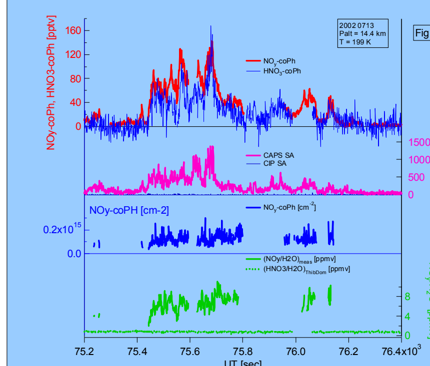

Fig. 4b

2002 0719: For this cloud pass (Fig 5a, 20:20-20:22) at 12.7 km, **T = 212 K**, the interesting feature is how small the condensed phase amounts are. NO_y-coPh and HNO_3-coPh are in good agreement (Fig. 5b, 1st panel). Values are 5-15% of the FHH calculation (3rd panel) and are comparable to the solubility limit with the low values of 0.1-0.2 ppmv (4th panel), unlike any other cases examined. HNO_3, not shown, is a steady (within the noise) 100 pptv, or 0.2 x 10-7 torr, across the time plotted, both in and out of cloud. "Kinetic" lifetimes are a few minutes.

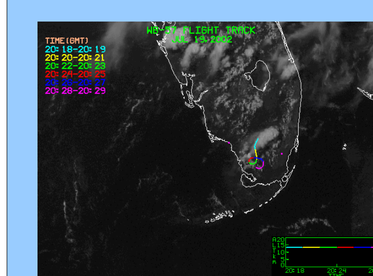

Fig. 5a

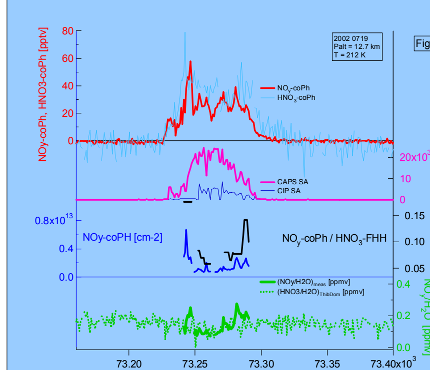

Fig. 5b

2002 0726: As the WB57 descended (Fig. 6a, 18:58-19:04) it experienced a temperature climb of 18 K, with **T = 197-215 K**. If HNO_3 were constant, the FHH model would predict a significant change in the surface density of HNO_3 on ice. This is not seen (Fig. 6b, 2nd panel). HNO_3 was not measured this day, but NO_y-Aft (Fig. 6b, 3rd panel) shows no suggestion of such a trend. "Kinetic" lifetimes (not shown) increase from 1500 s to 5000 s over the pass.

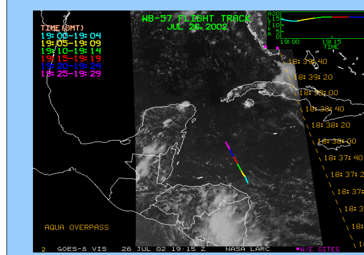

Fig. 6a

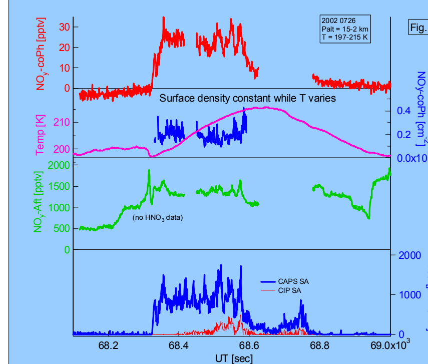

Fig. 6b

SUMMARY

- The measurements of condensed-phase NO_y and condensed-phase HNO_3 are usually in good agreement with each other, with exceptions especially on 0721 when HNO_3-coPh was larger (no compelling case for NO_y species other than HNO_3 condensing).
- For most cases the condensed-phase amounts are 10-100% of that calculated from the FHH model of Hudson et al. [2002], and they are generally much greater than that which could be explained by dissolution in the solid (except for the case on 0719). On 0721 (213 K) values are about equal to the FHH ones, on 0711 (204 and 208 K) they are about 50%, on 0719 (212 K) they are 5-15%.
- For the two cases studied with T < 200 K, very different behaviors were observed. On 0709, at the peak of the CAPS SA, the NO_y surface density is <~10^{-3} monolayer, while on 0713 ~0.2-0.4 monolayer was observed. The difference in the condensed-phase signals from the HNO_3 and NO_y instruments, and the greater sensitivity of the HNO_3 instrument to particles smaller than 4 μm suggests the possible presence of HNO_3-containing aerosols on 0709, which compete effectively with ice for the uptake of HNO_3.
- On 0726 the surface density of NO_y-coPh does not vary in correlation with the 18 K temperature change (197-215 K), as would be expected from the FHH model.
- Even allowing for the low values of uptake efficiency measured by Hudson et al. [2002], "kinetic" lifetimes are often in the range of 10-30 min, not too long in comparison with cirrus lifetimes.
- When gas-phase HNO_3 is near zero on 0709, the lack of detectable condensed-phase NO_y suggests that gas-phase HNO_3 is necessary for the occurrence of condensed-phase NO_y, that is, other species such as PAN may not be taken up by ice.
- The above conclusions are admittedly based on a limited number of cases. Future work will survey more cases (and give more attention to particle size spectra).

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